

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) HYDROPHILIC-HYDROPHOBIC PHOTON SENSITIVE MEDIUM

(71) We, HUGHES AIRCRAFT COMPANY, a Company organised under the laws of the State of California, United States of America, of Centinela Avenue and Teale Street, Culver City, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a medium for producing an image. The image is such that it is hydrophobic when unexposed and hydrophilic when exposed. The hydrophobicity-hydrophilicity difference is employed to produce a useful or visible image.

There are already known many silver halide media and other actinically sensitive media whereby a visible image is obtained by photon exposing the media and suitably developing and fixing the media to produce a visible image. The silver halide media and the processes employing the silver halide media are not the only other processes apart from the present process wherein physico-chemical amplification occurs in the media, to permit rapid image development from a fairly weak photon source. However, most of these known processes require a fairly long development time, or involve other complex processing.

Other types of photon sensitive media are fairly "slow" in that they do not employ physical or chemical multiplication, and require a much larger photon exposure before a usable image can result therefrom. For instance, processes used in diazo printing, and the media used in photoresists, are not of the nature which incorporate amplification of exposure, and thus they require very long exposures to be useful. Thus, the silver halide process requires considerable development time, while the remaining processes require a considerable exposure time, so that none of the prior art processes are capable of quickly producing a usable image from a normal photon source.

Additionally, regarding the use of photo-

sensitive materials as a master lithographic and other printing processes, most of the conventional photosensitive materials are negative-working in that they produce a reversal of tones, whereby photon exposed areas are dark when printed and the nonexposed areas are light. This requires the additional step in processing of preparing an intermediate negative in order to produce a final positive print. Also, the conventional presensitized printing plates do not have any ability to print grey tones, but print only black and white. This requires the additional complication of utilizing a half tone screen, to reproduce grey tones.

This invention is directed to the discovery of new classes of hydrophobicity inducing agents, useful in preparing a hydrophilic-hydrophobic photon-sensitive medium more particularly but not exclusively water-repelling agents, for example silicones, fluorocarbons or organic acids containing two to twenty-four carbon atoms. The invention also relates to processes utilizing aqueous liquids to form images on the photon-developed medium.

The present invention provides an image recording medium which is hydrophobic when unexposed and hydrophilic when exposed to photons, ions or electrons for producing an image corresponding to the exposure, which medium comprises a film-forming binder in which are substantially uniformly dissolved or dispersed:

a) a radiation-sensitive material sensitive to electrons, ions or photons and selected from the oxides of zinc, titanium, tantalum, indium, magnesium, germanium, tin and bismuth, sulphides and selenides of calcium, zinc, cadmium, iron and indium, boron nitride, calcium tungstate, beryllium aluminide, lithium carbonate, zinc carbonate, cadmium niobate, lithium niobate, anthracene and cesium-activated calcium-magnesium silicate and mixtures thereof;

b) a sensitization enhancing material selected from the following: copper chloride, copper (II) acetylacetonate, bismuth trioxide,

[Price 25p]

a mixture of cuprous chloride and the trimethylamine salt of tetracyanoquinomethane, cuprous chloride and copper (II) acetylacetonate, a mixture of copper formate and cuprous chloride, cupric sulphate, cupric chloride dihydrate, cupric bromide, cuprous sulphite, cupric thiocyanate, cuprous sulphide, cupric molybdate, cupric lactate, cupric formate, copper p-toluene sulphonate, cupric salicylate, cupric lineolate, cupric acetate, glycine cupric salt, cupric stearate, cupric tartrate, cupric citrate, d,l-malic acid copper salt, cupric oxalate, bis - (ethyl acetoacetato) copper, bis - 1 - phenyl - 1,3 - butanedione) copper, cupric dimethyl dithiocarbamate, cuprous sulphate- $\beta$ -naphthol, cuprous acetoacetate, silver benzotriazole, silver nitrate, silver fluoride, silver oxide, and gallium (III) nitrate; and

c) a hydrophobicity inducing agent selected from the following: a liquid or solid polymer formed from tetrafluoroethylene, chlorotri-fluoroethylene, fluorinated ethylene-propylene, vinylidene fluoride or hexafluoropropylene; fluorinated organic acid salts including the copper salts of heptafluorobutyric acid, per-fluoro-octanoic acid, pentafluoropropionic acid, p - fluorophenyl - acetic, 2 - hydroxy - hexa-fluoroisobutyric acid; a saturated aliphatic acid having a carbon content from  $C_{10}$ — $C_{17}$  or  $C_{19}$ — $C_{24}$  or unsaturated aliphatic acid having a carbon content from  $C_{10}$  to  $C_{13}$ , a fatty acid having a carbon content from  $C_{16}$  to  $C_{22}$  including palmitic acid, oleic acid, linoleic acid and linolenic acid, naphthenic acid; polydimethyl siloxane, silane modified silica or copper salt of fluorinated alkanolic acid.

On selective exposure of the medium, a hydrophilic image is formed supported and surrounded by hydrophobic non-image or background areas.

The present invention also provides a method of producing a medium as described above, which comprises forming a mixture of the film-forming binder, the photo-sensitive material, the sensitization enhancing metal compound and the hydrophobicity inducing agent, and forming a continuous solid film from the mixture.

The materials may be dispersed in a film forming binder to form a film which may be either self supporting or may be supported upon a suitable substrate. A dispersion of the materials in the binder may be formulated by forming a liquid dispersion of the agents, materials and binder in a liquid, suitably a solvent for the film-forming binder. After thorough mixing, the film is formed as a self-supporting film or as a coated film and is permitted to dry. In such a state, the medium is photosensitive and hydrophobic and is ready for further processing in accordance with the invention.

The hydrophilic, photon-sensitive medium in accordance with the invention, consists of a

material which is sensitive to the impingement of radiation, a metallic compound which is a sensitization-enhancing agent, a material which selectively renders the medium hydrophobic or hydrophilic in accordance with the photon exposure and a binder for forming a solid solution or dispersion of these ingredients in the form of a film. In some cases the strength of the binder is sufficient to form a self-supporting film and in other cases the film is supported on a substrate.

The substrate is a passive structure which does not enter into the activity of the photon-sensitive medium, except to act as a supporting structure, substrate or carrier. Therefore, the role of the substrate is entirely physical and mechanical as far as the practice of the invention is concerned. Suitable support substrates may be formed of almost any material and may partake of almost any geometry. Thus, paper, and especially paper in the form of a tape, may serve as suitable support substrate and is particularly desirable because of its flexibility. A number of synthetic polymer composition materials are also suitable. For example, the substrate may be formed of thermoplastic or thermosetting materials such as polyethylene, polypropylene or styrene polymers, for example butadiene-styrene, polyesters such as polyethylene-terephthalate, acrylics such as methyl methacrylate, or cellulose derivatives such as cellulose acetate.

Flexible substrates permit processing from continuous roll supplies and conformation of the finished and developed media to, for example, arcuate shaped printing rolls. However, rigid substrates can just as well be used in some cases, for example for flat planographic printing or etching of printed circuit boards. Rigid substrates can be formed of synthetic polymer composition materials, glass, metal, ceramic, refractory or impregnated woven sheets such as impregnated phenolic printed circuit boards.

A satisfactory binder or matrix for forming the film of photosensitive media, according to the invention, may be any of the well known film-forming synthetic organic resins, particularly those formed from vinyl and/or diene monomers or their mixtures. The vinyl monomers may be ethylene, propylene, vinyl chloride, vinylidene chloride, vinyl esters such as vinyl butyrate and preferably are vinyl aromatics such as styrene or vinyl toluene. The diene monomers may be  $C_4$  to  $C_{10}$ , dienes such as butadiene, isoprene, methyl butadiene, or dimethylbutadiene. A typical binder of the styrene-butadiene type of copolymer which has been used successfully in the practice of the present invention, is one identified as "pliolite (Registered Trade Mark) S-7" (30% solids in toluene), manufactured by Goodyear Tire and Rubber Company, Chemical Division, Akron, Ohio. Other satisfactory

matrix materials are polystyrene, chlorinated rubber, polyvinylidene chloride, and polyvinyl butyral.

5 A solid dispersion or solution of the active materials may be within the matrix or binder and may be formed by any of the well-known techniques such as by adding a solution or dispersion of the materials to a solution or emulsion of binder particles, intimately mixing and then drying. Suitably, the binder is dissolved in a solvent to form a solution of reduced viscosity and the solid materials are added to the solution and dispersion therein. Any suitable solvent may be utilized to adjust the miscibility and spreadability of the dispersion. For styrene-butadiene resins such as Pliolite, the solvent may be an aromatic such as toluene or an ether such as dioxane. Other solvents for butadiene-styrene resins are chlorinated hydrocarbons and some ketones.

25 The solvent or dispersion may be cast onto a release surface to form a self-supporting film or the material may be applied to the surface of a substrate, support or backing material by flow coating, dipping, spraying, doctor blade or other conventional coating operation. On removal of the solvent, the media is ready for further processing to form images by exposure and development.

30 The radiation material suitable for use in the practice of the present invention, appears to include materials which are classifiable as either photoconductive or photoemissive. The material is sensitive to the impingement of electrons, ions or photons.

35 Preferably, zinc oxide is used as the radiation-sensitive material.

40 The amount of sensitization-enhancing material incorporated in the film forming may be varied over wide ranges. Ratios of sensitization-enhancing agent to photosensitive material from  $10^{-3}$  to  $10^{-1}$  by weight have given substantially equivalent results with no discernible differences.

45 The material which renders the radiation-sensitive medium hydrophobic according to this invention is a water-proofing agent. The said material may be a polydimethylsiloxane, which can be a liquid or solid polymer. An exemplary commercial available liquid material is G.E. "SR-82" silicone resin. Another form of hydrophobic silicone is a hydrophobic silicon dioxide aerosil (Registered Trade Mark) obtained by reaction with a chlorosilane. The chlorine reacts with surface silanol groups to attach the silane to the silica particle. Typically, dimethyl chlorosilane attaches to silica to provide a carbon content of 0.8 to 0.9% per 100 m<sup>2</sup> of product. An exemplary commercial product is (Degussa) "Aerosil R-972".

60 As stated hereinbefore, the hydrophobicity inducing agent may be a saturated or unsaturated aliphatic acid, for example naphthenic

acid. Commercial naphthenic acid is a mixture of saturated cycloaliphatic acids, predominating in monocyclic, monocarboxylic acids containing a substantial percentage of materials having a carbon content from C<sub>10</sub> to C<sub>18</sub>. The acids present in naphthenic acid typically have molecular weights in the range of 180 to 350. Organic acids that may also be used are saturated aliphatic acids having a carbon content from C<sub>10</sub>—C<sub>17</sub> or C<sub>19</sub>—C<sub>21</sub>, or unsaturated aliphatic acids having a carbon content from C<sub>10</sub> to C<sub>24</sub> preferably a fatty acid having a carbon content from C<sub>16</sub> to C<sub>22</sub> such as palmitic acid, oleic acid, linoleic acid and linolenic acid.

The hydrophobicity agent is preferably present in the range of 0.05 to 10 grams, preferably below 5 grams based on 100 grams of film forming solids. If the agent is utilized in the presence of another hydrophobicity agent such as the hydrated salts, fatty acid salts or water containing materials the normal amount of each material is reduced to a level to provide satisfactory but not excessive hydrophobicity.

The sensitive material and the sensitization enhancing material are both usually in a finely comminuted form. The dry powder materials are mixed together with the hydrophobicity inducing material and with the desired binder and solvent, for example, toluene, suitably in an orbital ball mill, jar mill or vibratory mill until thorough dispersion of the ingredients is achieved. The mixture is then applied to a suitable substrate by conventional knife-coating equipment so as to form a film thereon having a wet thickness of 25—100 microns. For example, in general, the dry thickness of the film varies between 25 to 50% of the wet thickness. Upon drying, the film is ready for use.

The selected hydrophilicity is utilized, in accordance with the invention, to provide aqueous developed images which are useful for selectively attracting water or water bearing materials to the nucleated image or in the converse for rejecting hydrophobic materials from the aqueous developed areas. The aqueous developer may carry a solution or dispersion of dye or pigment so that when water is selectively adhered to the hydrophilic areas of the medium, the dye or pigment deposits thereon to form a visible image. When dry, the developed print is a positive reproduction of the original information design, indicia. In the case of colloidal pigments suspended in water, the colloid is firmly attached to the surface in the hydrophilic exposed and developed areas so that it properly remains in place after the aqueous solution has evaporated. Of course, the hydrophobic areas repel the water so that there is no dye or pigment absorption or deposition.

Following the exposure and development in an aqueous media, tenaciously adsorbed

water images are formed on the surface of the hydrophilic exposed areas. This water image will repel hydrophobic materials such as oil-based ink or molten wax. With the subsequent application of a hydrophobic lithographic ink, the ink will be repelled by the hydrophilic water developed image areas and will be retained by the hydrophobic background areas. A lithographic printing process results by transferring the ink image to a sheet of paper either directly or by means of an intermediate rubber blanket. The process of alternatively water wetting and inking can be repeated to produce multiple prints on any conventional lithographic press.

If the hydrophobic compound is molten wax, on cooling and solidification of the wax, as in-depth wax image is formed which could be used as a gravure printing plate for an intaglio printing process, or alternatively, the wax image could be used as an etchant-resist for making a photoresist printed circuit board.

The photon activated recorded latent surface is also selectively sensitive to the deposition of metallic vapour. When a metal is delivered to the surface in vapour form, the impinging vapour atoms will deposit selectively on the nucleation site because of the higher adsorption energy. On the unexposed areas, the re-evaporation rate will nearly equal the incident rate and there will be no deposition, while on the nucleation sites the re-evaporation rate will be very low. The vapourous metal is preferably selected to have increased hydrophilicity and lyophobicity and is suitably zinc, cadmium or mercury. The vapourous metal coated media when wet with water exhibits increased resolution and better continuous-tone-reproduction.

All of the aforementioned processes may be utilized with the water developed exposed hydrophilic image or additionally with the metal vapour developed image.

In another variation of utilizing the hydrophilic properties of the exposed image, a photoresist may be directly produced by further developing the nucleated image with a material that forms a hard image-wise deposit. For example, potassium dichromate when applied to the recorded latent image and "developed" by exposure to ultraviolet radiation, forms such a deposit. The hard and impermeable image will act as a resist when the material is dipped in a solvent that dissolves the binder for the sensitive layer thereby exposing the base material. The solvent etched assembly could be used directly as a printing plate or as a photoresist preliminary to chemical milling with an etchant suitable for the base material.

A number of embodiments of the invention will now be described in detail by way of Example only with reference to the accompanying drawings in which:—

Figure 1 shows diagrammatically a photon

exposure aqueous development imaging system with a front housing cover removed, employing a medium according to the invention.

Figure 2 shows diagrammatically a lithographic printing process.

Figure 3 shows diagrammatically a deposition process, and

Figure 4 shows diagrammatically an etching process.

Referring to Figure 1, an aqueous developing imaging system employing the hydrophobic-hydrophilic media, according to the invention, is generally indicated as the device 10. The device 10 comprises a housing 12 which is preferably light-tight, because of the photon sensitive character of the medium employed therein. However, for purposes of illustration, the near side cover of the device 10 has been removed so that the interior can be seen. The housing 12 contains a first chamber 14 which functions as a storage chamber for the medium, and if desired, can include coating equipment for applying the medium to a substrate 28. The chamber 14 is connected to a second chamber 16 through light trap 18. Similarly, chamber 16 is connected to a chamber 19 through light trap 22. Then the medium leaves chamber 19 through a light trap 23 and enters a third chamber 20. The medium leaves the device 10 through a light trap 24.

Within chamber 14, a storage reel 26 furnishes a supply or substrate 28 which is lead under coater 30 containing a supply of media, and around guide rolls 32 and 34 so that it can pass through light trap 18 into chamber 16. The coating is permitted to dry during its passage around guide rolls 32 and 34 and, if desired, a forced air dryer can be incorporated within chamber 14 facing the top surface of substrate 28, coated with the medium. Since the medium being applied to the substrate is photo-sensitive, the coating is carried out in chamber 14 which has a light level sufficiently low that exposure and activation of the media does not take place. It is again noted that the coating process need not be an integral part of the exposing and developing system. The substrate may be coated many months in advance of the actual use and a reel of coated presensitized media inserted into chamber 14 and wound onto the appropriate drive and guide rollers.

The coated and dried medium is now ready for exposure which occurs within the second chamber 16. In chamber 16 the medium is exposed by light source 36 which is powered by power supply 38. Light source 36 can be a suitable projector which projects an image upon the sensitive surface of the medium in which case the medium 28 is held stationary for an adequate length of time, during exposure. On the other hand, light source can be a suitable scanning light beam

which scans transversely to the direction of motion of medium 38, in which case the advance of medium passed the transversely scanning light source can be at an appropriate rate to provide the necessary spacing longitudinally of the medium 28.

The light sensitivity of the media will depend on the composition thereof, but the coating given in Example 1 below, typically has an exposure range from unexposed to fully exposed over an exposure range of ultraviolet light from 10 ergs/cm<sup>2</sup> to 1000 ergs/cm<sup>2</sup>. The medium is completely hydrophobic before exposure to the minimum value of light energy given above, and is hydrophilic when subjected to the full exposure. At the intermediate levels of exposure, certain of the active sites are exposed and render particular areas at the sites hydrophilic so that the materials dissolved in water are carried by water to be deposited thereon. The intermediate range of exposure thus result in closely spaced hydrophobic and hydrophilic areas, so that irregular or discontinuous images result.

After exposure, the medium 28 passes through light trap 22 into an optional third chamber 19. If desired, the exposed activated image areas of the media 28 can be coated with metal within this chamber, or, the metal coating may be accomplished simultaneously with exposure within the chamber 16. As a result of the exposure to electrons, ions or photons, the surface of the media 28 is provided with a latent image comprising a number of nucleating sites in a pattern corresponding to the indicia to be reproduced. When metal vapour is applied to the surface of the exposed media, atoms or molecules from the vapour are selectively attracted to and retained by the nucleated areas comprising the latent image. Each atom in a nucleating site may capture as many as 10,000 atoms from the vapour. The necessary vapour is supplied from a source 25 usually associated with a controlled heater means 27. Generally, the vaporous metal developer materials are metals for example zinc, cadmium or mercury in bulk or powder form in a crucible or in the form of a wire. The metal vapour may also be supplied in the form of a reducible or thermally decomposable metal compound, for example a metal carbonyl compound.

Metal vapour development takes place under the usual conditions governing the decompositions of metal in vacuum. Thus, chamber 19 is placed under vacuum and the media 28 is spaced a distance from the vapour source 25 not more than the mean free path existing in the chamber at given conditions. Pressures in the ranges of 10<sup>-1</sup> to 10<sup>-4</sup> torr may be used for this purpose. Inert gases, for example helium-argon, may also be employed and introduced into the chamber to modify the velocity at which vapour molecules reach

the surface permitting a greater degree of control of image contrast.

After exposure and optionally after metal vapour development, the medium 28 passes through light trap 23 into aqueous development chamber 20 and from chamber 20 the medium 28 passes out of the devices 10 through light trap 24. Within the chamber 20 the medium passes around guide rolls 40, 42 and 44; during passage around guide roll 42 the medium is submerged within an aqueous bath 46 and the liquid is selectively deposited on the hydrophilic image areas. If the aqueous bath 46 carries dye or pigment, the colouring matter will be deposited on the hydrophilic image areas. The media 28 leaves chamber 20 with an aqueous developed image formed on the hydrophilic exposed areas, regardless of whether it has been developed with metall vapour in chamber 19.

It should be understood that complete immersion in liquid is shown for purposes of illustration and that this is only one of many suitable methods for applying the developer. Other satisfactory methods include surface application of the liquid from a revolving roller, spray application and other well known means of solution application.

The aqueous developing time for this process is characteristically very short. The required time will vary as a function of the concentration of the hydrophobicity-inducing agent in the medium (being less for smaller concentrations thereof), as a function of the concentration of sensitization agent, being less for smaller concentrations thereof, as a function of ball milling time used to blend the ingredients (being less for longer ball-mill time), and as a function of developer temperature (being less for higher developer temperatures). Depending on the aforementioned variables, developing time may vary from 0.1 second up to 20 seconds. Typical developing times are from 0.5 to 5 seconds at 70° F.

Following development, no further processing is required. However, to facilitate handling of the product, it may be desirable to use forced-air or radiant drying (or both) to dry the excess developer solution adhering on the surface of the medium.

As the medium comes out of light trap 24, it is ready for inspection and handling.

The following examples are intended to illustrate the preparation of the recording media of the invention, its exposure and development.

#### EXAMPLE I.

A large number of coatings were made based on the same basic formula as follows:

Zinc Oxide (Photox 801)	50—75 grams
Pliolite S-7	18 grams
Toluene	50—80 cc
Methanol	4 cc

5 Various sensitizers and hydrophobicity-inducing agents were then added to this basic formula and the ingredients combined in a 500 cc gross-capacity aluminium oxide ball mill with 100 19 mm diameter agate balls, and milled on a planetary ball mill for 45 minutes. The media was then coated in a

wet thickness of 25 to 100 microns on a substrate of aluminized polyester film base or other suitable support. The resultant coatings were tested for hydrophobicity. The addenda and results of the test coatings are given in Table I.

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TABLE I.

15	Tape Composition	Sensitization agent	Hydrophobicity Agent(s)	Resulting Hydrophobicity
	1a	Copper acetylacetonate (0.1g)	Naphthenic Acid (0.5g)	Poor
	1b	Copper acetylacetonate (0.10g)	Naphthenic Acid (1.0g)	Poor
20	2a	Copper acetylacetonate (0.10g)	Linoleic Acid (0.25g)	Fair
	2b	Copper acetylacetonate (0.10g)	Linoleic Acid (0.50g)	Fair
25	2c	Copper acetylacetonate (0.10g)	Linoleic Acid (1.0g)	Good
	2d	Copper acetylacetonate (0.10g)	Linoleic Acid (2.0g)	Good
	3	Cuprous Chloride (0.10g)	Aerosil R-972 (0.30g)	Good
30	4	Cuprous Chloride (0.10g)	Formalin (8ml) and Aerosol R-972 (0.3g)	Good
	5	Cuprous Chloride (0.10g)	G.E. SR-82 Silicone Resin (1.0g)	Fair

40 It is seen from the Table that best results are achieved with linoleic acid present in an amount of 1 to 2 grams or with the silane treated silica material. The media according to the examples can be exposed with approximately 300 ergs/cm<sup>2</sup> of 3625 Å ultraviolet radiation. Development can then consist of a one second surface application of a water suspension of colloidal graphite or suitable dyes. A graphite developer can be prepared by dispersing 83 grams of Acheson Colloids "Aquadag (Registered Trade Mark) (22% solids in water)" in 1 litre of deionized water.

50 The alkalinity of the developer can be adjusted with ammonia or acetic acid to produce a pH between 8 and 11. The higher pH produces more rapid but less selective development.

55 The exposed sheet can also be developed by immersion for 1—20 seconds in tap water or preferably in a lithographic fountain solution. Referring now to Figure 2 of the accompanying drawings, a length 60 of the medium 28 developed, in accordance with Figure 1, is removed and cut to printing plate size. The plate 60 is applied to a printing roller 62. Tank 64 contains fountain solution 66 such as Addressograph-Multigraph (AM) Multilith (Registered Trade Mark) "Repelex" (Registered Trade Mark) fountain solution (concentrate diluted 1:30 with deionized

water). Tank 68 contains an oil-based printing ink 70 such as Von Son Holland "Quickset Printing Ink" or AM "MLS Series Multilith Ink". Rollers 72 and 74 apply the respective fountain solution 66 and ink 70 to the surface of the printing plate 60.

A source of paper 75 from roll 76 passes around guide roll 78 and is pressed against the surface of the printing plate 60 by means of press roll 80 and then passes by guide roll 82 before being rewound on take-up roller 84. On each revolution of the printing roller 62, the fountain solution 66 will selectively adhere to the exposed hydrophilic areas of the plate 60 and therefore the subsequently applied ink 70 will be rejected by these areas to provide a clear and sharp background for the finished prints. The ink accepted by the non-exposed areas is transferred to the paper 75 passed in contact with the printing plate 60.

Multilith prints made from a hydrophilic hydrophobic medium, according to the invention, exhibit greatly improved contrast and lack of ink pick-up in the background areas. A press run is capable of producing several hundred clear legible copies with good resolving power. Furthermore, the Multilith-produced prints do not show the characteristic fill-in of circular shapes such as the centre of the letters "O" and "e" which is typical

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of aqueous development by dipping. This is attributable to the printing press breaking the bubbles by pressure of the rollers.

5 In the case of media subjected to vacuum development with metal vapour such as zinc in chamber 19 of Figure 1, the copies produced are somewhat sharper and exhibit a degree of direct half-tone reproduction without the use of half-tone screens.

10 A further process utilizing the aqueous developed media, prepared in Figure 1 is illustrated in Figure 3. In this process, a hardenable oleophilic compound is applied to the aqueous developed exposed medium. The oleophilic material hardens to form an impermeable image having a relief image corresponding to the exposed portions of the medium. Referring now to the drawings, the exposed medium 28 enters chamber 20 where it passes around guide roll 42; it is aqueous developed within the water bath 46.

20 The developed media 28 then passes through light-trap 24 into light-tight chamber 90. The media passes around guide rolls 91, 92 and 94 within chamber 90. As the medium passes around roll 92, it is submerged within a liquid oleophilic compound, for example hot wax 96. The wax is repelled by the oleophobic water-adsorbed exposed image areas, but it builds up upon the unexposed portions of the sensitive medium on web 28. The hard wax is cooled by any convenient means such as by cooling immersion roller 92 so that a solid wax image is built up upon the unexposed areas. The medium leaves chamber 90 through a trap 98.

35 The medium having the built up image prepared in accordance with the last figure can be utilized as a gravure printing plate to produce copies. A water-base ink when applied to such a plate will adhere to the relieved hydrophilic areas, but will be repelled by the built-up wax areas. Furthermore, since the image areas are depressed, the ink can be wiped off the raised non-image areas. After wipe-off, the ink can be transferred by pressing the plate against a transfer sheet, for example paper. The gravure printing plate can be repeatedly reinked with gravure ink and printed against paper. In such a case a portion of the web corresponding to the pattern to be printed in multiple copies is severed from the web and inserted in a press as a printing plate for producing multiple copies.

55 It should be noted that the wax image can be used as an etchant resist. In such a case, the substrate should be an etchable material, for example a film of metal or a film of metal laminated to an inert support, suitably a polyester, for example, "Mylar" (Registered Trade Mark). The etchant can be any suitable solvent for the etchable substrate which does not attack the wax layer, and may be an acid or alkali material oxidiz-

ing agent or reducing agent. The etching process may also be operated on the severed sheets of media in a batch type of operation rather than the continuous operations that have been illustrated.

70 A process which yields a photo-resist directly from the photon exposed media of Figure 1 without the need for forming a relief image is illustrated in Figure 4. The photon exposed media 28 passes through light trap 23 into light-tight chamber 20. The aqueous media 46, in this case, contains a compound that forms a hard impermeable deposit upon the hydrophilic exposed areas. An aqueous solution of potassium dichromate is suitable for this use. The dichromate treated media leaves chamber 20 through light trap 24 and enters chamber 102.

85 Within chamber 102, the treated media is exposed overall to ultraviolet radiation from a high intensity ultraviolet lamp 103 which acts to cross-link, polymerize or otherwise harden the dichromate coated, exposed areas. The treated media leaves the chamber 102 through light trap 104 and enters chamber 106. Within chamber 106 the media passes around guide rolls 108, 110 and 112. The roll 110 is at least partially immersed within a bath 114, which contains a solvent for the media. The solvent dissolves the film-forming binder of the photosensitive coated film 28 so that the web beneath the unexposed areas is removed to expose the underlying portions of the web substrate. A suitable solvent for the film forming binder is toluene.

100 As the web 28 leaves chamber 106 through light-trap 115, the originally photon unexposed areas of the web are unprotected while the photon-exposed areas are protected both by a layer of the sensitive material and a layer of the hard impermeable deposited material. The web 28 may then be delivered to a tank 116 containing a bath of etchant 118. The web passes over rollers 120, 122 and 124. Rollers 122 is again partially submerged within the bath 118 and as the web passes over this roller the etchant removes material from the unprotected areas of the tape corresponding to the photon-unexposed areas. This process can be used for preparing printing plates or in processes of chemical milling. Again the process may be carried out in a step-by-step batch basis on separate sheets of material prepared on rigid substrates.

#### WHAT WE CLAIM IS:—

1. An image recording medium which is hydrophobic when unexposed and hydrophilic when exposed to photons, ions or electrons for producing an image corresponding to the exposure, which medium comprises a film-forming binder in which are substantially uniformly dissolved or dispersed:

a) a radiation-sensitive material sensitive to



electrons, ions or photons, and selected from the oxides of zinc, titanium, tantalum, indium, magnesium, germanium, tin and bismuth, sulphides and selenides, of calcium, zinc, cadmium, iron and indium, boron nitride, calcium tungstate, beryllium aluminide, lithium carbonate, zinc carbonate, cadmium niobate, lithium niobate, anthracene and cesium-activated calcium-magnesium silicate and mixtures thereof;

b) a sensitization enhancing material selected from the following: copper chloride, copper (II) acetylacetonate, bismuth trioxide, a mixture of cuprous chloride and the trimethylamine salt of tetracyanoquinomethane, cuprous chloride and copper (II) acetylacetonate, a mixture of copper formate and cuprous chloride, cupric sulphate, cupric chloride dihydrate, cupric bromide, cuprous sulphide, cupric thiocyanate, cuprous sulphide, cupric molybdate, cupric lactate, cupric formate, copper p-toluene sulphonate, cupric salicylate, cupric lineolate, cupric acetate, glycine cupric salt, cupric stearate, cupric tartrate, cupric citrate, d,l-malic acid copper salt, cupric oxalate, bis-(ethyl acetoacetato) copper bis(1-phenyl-1,3-butanedione)copper, cupric dimethyl dithiocarbamate, cuprous sulphate- $\beta$ -naphthol, cuprous acetoacetate, silver benzotriazole, silver nitrate, silver fluoride, silver oxide, and gallium (III) nitrate, and

c) a hydrophobicity inducing agent selected from the following: a liquid or solid polymer formed from tetrafluoroethylene, chlorotrifluoroethylene, fluorinated ethylene-propylene, vinylidene fluoride or hexafluoropropylene; fluorinated organic acid salts including the copper salts of heptafluorobutyric acid, perfluorooctanoic acid, pentafluoropropionic acid, p-fluorophenylacetic, 2-hydroxy-hexafluoroisobutyric acid, trifluoroacetic or 3-trifluoromethyl-3-hydroxybutyric acid; a saturated aliphatic acid having a carbon content from  $C_6$  to  $C_{21}$  or  $C_{21}$  or an unsaturated aliphatic acid having a carbon content from  $C_6$  to  $C_{21}$ , a fatty acid having a carbon content from  $C_{16}$  to  $C_{22}$  including palmitic acid, oleic acid, linoleic acid and linolenic acid, naphthenic acid, polydimethyl siloxane, silane modified silica or copper salt of fluorinated alkanolic acid.

2. A medium as claimed in claim 1, wherein the ratio of sensitization-enhancing agent b) to radiation sensitive material a) is from  $10^{-2}$  to  $10^{-1}$  by weight.

3. A medium as claimed in claim 1 or 2, wherein the hydrophobicity inducing agent c) is present in a range from 0.05 to 10 grams, based on 100 grams of the solid content of the medium.

4. A medium as claimed in claim 3, wherein the hydrophobicity inducing agent c) is present in an amount below 5 grams based on 100 grams of the solid content of the medium.

5. A medium as claimed in any one of claims 1 to 4, wherein the binder is a film-forming synthetic organic resin.

6. A medium as claimed in claim 5, wherein the binder is a resin formed from vinyl and/or diene monomers or from their mixtures.

7. A medium as claimed in claim 6, wherein the vinyl monomer used is styrene or vinyl toluene.

8. A medium as claimed in claim 6 or 7, wherein the diene monomer used is butadiene, isoprene, methyl butadiene or dimethyl butadiene.

9. A medium as claimed in claim 1 and substantially as described herein, with reference to the Examples.

10. A method of producing a medium as claimed in any one of claims 1 to 9, which comprises forming a mixture of the organic film-forming binder, the radiation-sensitive material sensitive to electrons, ions or photons, the sensitization enhancing material and the hydrophobicity inducing agent, and forming a continuous solid film from the mixture.

11. A method as claimed in claim 10, wherein the film is formed on a substrate.

12. A method as claimed in claim 11, wherein the substrate is paper or a synthetic polymer composition.

13. A method of producing an image on the medium as claimed in any one of claims 1 to 9, comprising exposing selected areas of the medium to photons and treating the medium to photons and treating the medium with an aqueous developer to make the exposed areas visible or transferable.

14. A method as claimed in claim 13, wherein the medium is treated with an aqueous developer carrying visible materials so that the visible materials are deposited on the exposed areas of the medium.

15. A method as claimed in claim 14, wherein the visible materials are colour particles.

16. A method as claimed in claim 13, wherein a vaporous metal is applied to the medium to deposit the metal on the exposed areas thereof.

17. A method as claimed in claim 16, wherein the metal is zinc, cadmium or mercury.

18. A method as claimed in claim 13, comprising coating the medium on an etchable metal backing and treating the medium with the aqueous developer containing a metal etchant.

19. A method as claimed in claim 18, wherein the treating step is followed by applying a solvent to the medium to dissolve the medium from the metal backing.

20. A method as claimed in claim 18, wherein the treating step comprises applying to the medium the aqueous developer containing a compound which hardens; drying the aqueous



5 developer so that a hard deposit is formed on the hydrophilic areas of the medium; applying to the medium a solvent to dissolve areas of the medium which are unprotected by the hard deposit; and applying an etchant to the resultant exposed etchable metal to etch away at least a portion of the exposed etchable metal.

10 21. A method as claimed in claim 20, wherein an aqueous solution of potassium dichromate is applied to the medium.

15 22. A method as claimed in claims 20 or 21, wherein the solvent used for dissolving areas of the medium that are unprotected is toluene.

20 23. A method as claimed in claim 13, wherein the treating step is followed by applying to the medium an oil base ink so that the ink is positioned on the hydrophobic areas of the medium and is rejected by the absorbed water covering exposed hydrophilic areas of the medium; and imprinting the ink upon a base by pressing the medium having the oil base ink on the hydrophobic areas thereof against the base.

24. A method as claimed in claim 13, wherein the treating step comprises placing ink upon the medium in accordance with the pattern determined by the hydrophilic and hydrophobic areas of the medium.

25. A method as claimed in claim 24, wherein the placing of ink comprises forming a water film on the hydrophilic areas of the medium; forming a built-up wax layer on the hydrophobic areas of the medium; filling the hydrophilic areas between the built-up wax with gravure ink; and printing a base by pressing the medium against the base.

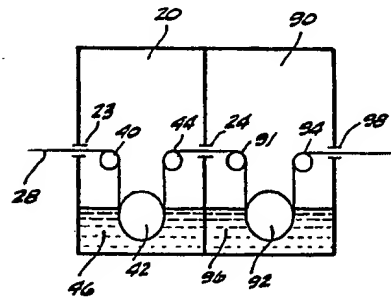
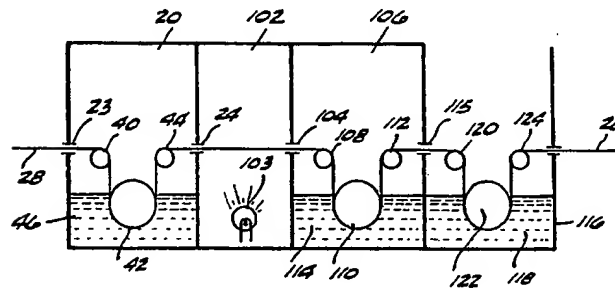
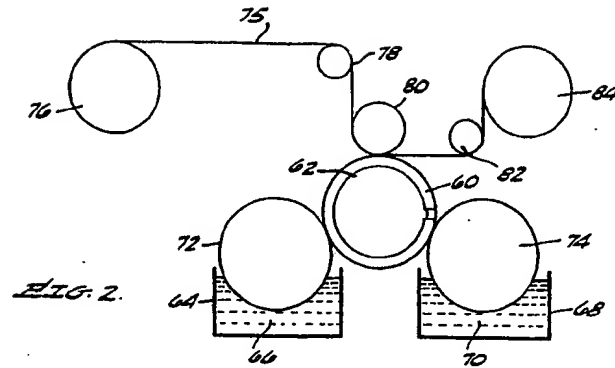
26. A method of producing an image on the medium as claimed in claim 1, substantially as described herein with reference to the accompanying drawings.

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